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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Stoyanov, O. V. , Deberdeyev, R. Ya. , Shmakova, O. P. , Bogdanova, S. A. and Zaikov, G. E.(2000) 'The Structure and Diffusion Properties of Polyethylene Coatings', International Journal of Polymeric Materials, 47: 2, 477 – 485

To link to this Article: DOI: 10.1080/00914030008035081

URL: <http://dx.doi.org/10.1080/00914030008035081>

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The Structure and Diffusion Properties of Polyethylene Coatings

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(Received 10 May 1999)

Sorption and diffusion properties of polyethylene coatings have been studied as a function of their preparation conditions. The temperature conditions of coating formation have been shown to affect substantially the structure as well as sorption and diffusion characteristics of polyethylene.

Keywords: Polyethylene; coatings; sorption; diffusion; preparation

INTRODUCTION

Sorption and diffusion properties of coatings prepared on crystallizing polymers are primarily determined by structural features, namely, the density, the crystallinity and internal tension level [1–3]. The migration of low molecular-weight substances passes through amorphous regions. In this case the density is one of the most important characteristics. Besides, the possibility of partial diffusant penetration through the defect regions of crystalline phase exists for such polymers as polyethylene. It is also suggested that intermediate regions bordering upon the crystallites make some contributions to the density and sorption ability changes of amorphous regions [3]. At the same time

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the existence of interface boundary layer has been revealed accompanying the coating formation on different substrates [4, 5]. In the case of crystallizing polymers the boundary transcrystalline layers (BTL) have a pronounced effect on the coating properties. Opinions differ widely on the estimating of BTL abilities as a diffusion barrier. According to [6] films of transcrystalline structure have mass transfer constants less than samples without BTL. On the contrary other authors [7] reasoned that BTL lead to mass transfer constant increasing. Moreover, BTL extent in coatings formed from crystallizing polymers is estimated differently by different authors [4, 8].

That is why we have investigated the effect of technological conditions of coating formation on diffusion properties.

The coatings were prepared on low density polyethylene (LDPE).

In the case of crystallizing polymers the boundary transcrystalline layers (BTL) have a pronounced effect on the coating properties.

That is why we have investigated the effect of technological conditions of the coating formation on the surface of various substrates on the change of their diffusion properties.

EXPERIMENTAL

The low density polyethylene (LDPE) was used (Tab. I). Polymer coatings were formed on the surface of metallic plates made of carbon steel. The thickness of the coatings was preassigned with the help of patternframe and varied from 350 to 400 μm . The cathodic peeling technique and the anodic electrochemical metal dissolution were used for the defectless separation of substrate and coating [5, 9]. The coating density was determined by the hydrostatic weighing method at 293 K

TABLE I LDPE characteristics

| | |
|---|-------|
| Density, kg/m^3 | 920 |
| Crystallinity, % | 42 |
| Melting temperature, $^{\circ}\text{C}$ | 108 |
| Molecular weight (viscosimetry) | 20000 |
| Content of $>\text{C}=\text{C}<$ double bonds (per 1000 carbon atoms) | 0,3 |
| Flow-melt index, g/10 min | 7,0 |
| Tensile fracture stress, MPa | 11 |
| Percentage elongation after fracture, % | 450 |
| Tensile yield point, MPa | 11 |

using ethanol-water mixture. Structure characteristics were determined by means of differential scanning calorimetry and radiography using a DRON-1 diffractometer [10]. The BTL thickness and the induction period of BTL formation were estimated on the face coating sections 30 μm thick with the help of polarizing microscope.

The integral diffusion coefficient \bar{D} of hexane was calculated using the initial portion of the coating swelling curve for the liquid phase with the help of Boltzman solution of the Fick equation [11]. \bar{D} of H_2O vapour was determined by the "glasses" method using the non-steady state portion of the kinetic curve [12]. \bar{D} of CO_2 was estimated by a certain technique using a HL-6 chromatograph [13]. The data obtained are close to the currently available data concerning this question [14].

THE RESULTS AND DISCUSSION

It has been established previously [5] that BTL existing in LDPE coatings on steel differ structurally from the basic block. Their extent changes extremely according to temperatural and temporal conditions of coating formation. The ability of such structures production at each specific temperature of the film formation is limited by the induction period reducing with increasing T (Fig. 1). The BTL thickness ranges

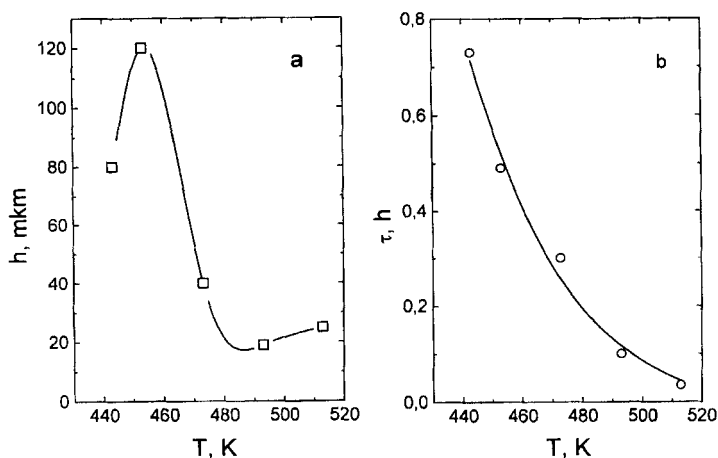


FIGURE 1 Extent of a transcrystalline layer (a) and induction period of its formation (b) vs. temperature of coating preparation.

up to 120 μm after film formation for 1 hour at 453 K followed by cooling to room temperature at the rate of 15 K/min.

BTL cause significant changes in the coating diffusive characteristics. Hexane \bar{D} is markedly smaller for BTL containing coatings than in the case of coatings without BTL formed identically (Fig. 2). To prepare BTL-free coatings the method used in [5] was applied. In both cases the curves for D pass through a minimum at 453 K.

It has been known that \bar{D} reduces with a rise of PE crystallinity φ_C [14]. However, in the case being considered, the value of φ_C for coatings containing BTL is closely related to φ_C for the samples without BTL and comprises 41 and 39%, respectively. At the same time the density of samples with BTL (930 kg/m^3) differs from those without BTL. The amorphous regions density was estimated using the equation:

$$d = d_C\varphi_C + d_a\varphi_a,$$

where $d_C = 1000 \text{ kg/m}^3$ is the density of the crystalline phase, d_a is the density of amorphous regions, $\varphi_a = 1 - \varphi_C$ is the amorphous regions content.

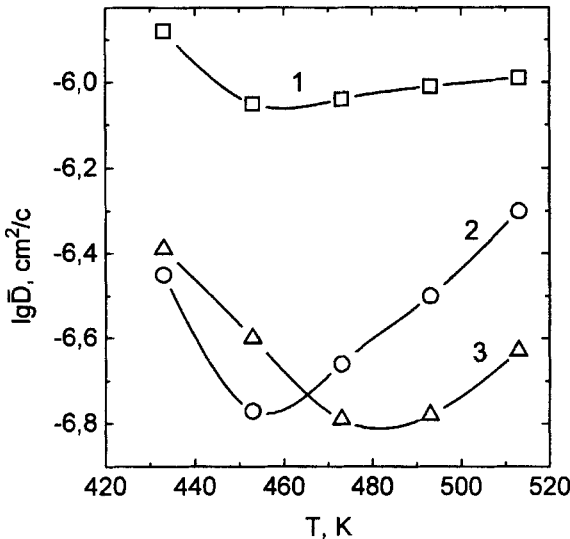


FIGURE 2 The effect of the temperature of coating formation on the hexane diffusion coefficient. 1, 3 – coating without a transcrystalline layer; 2 – coating with a transcrystalline layer; 1, 2 – air cooling at the rate of 15 K/min; 3 – water cooling at the rate of 130 K/min.

The value of d_a comprises 889 kg/m^3 for BTL containing coatings and 861 kg/m^3 for coatings without BTL. So the coating formation in transcrystallization conditions leads not only to structure ordering in boundary layers but to amorphous regions densification as well. It follows that D for BTL containing coatings significantly decreases.

The analysis of coating sorption capacity M^∞ and BTL extent points to correlation between them (Fig. 3). M^∞ falls with the increase in BTL thickness. As it was shown above, the density of amorphous regions of BTL containing coatings is higher than was the case free of BTL. The BTL thickness is linear with M^∞ , it follows that the amorphous regions density and BTL thickness change in a similar way since φ_C varies only slightly. The value of M^∞ for hexane in the case of BTL coatings is less than those reported in the currently available data for 39–45% crystallinity [14]. It supports the assumption that BTL formation is followed by the sealing of polymer amorphous regions. So M^∞ when extrapolated to zeroth value of BTL thickness was $0.045 \text{ g hexane/g PE}$ at crystallinity more than 60% and integral density is of the order of 940 kg/m^3 . At the same time, φ_C corresponding to a maximum of BTL extent is of 41% at the density of 930 kg/m^3 . It should be noted that adequate changes in structural characteristics such as elementary cell parameters and \bar{D} of hexane is

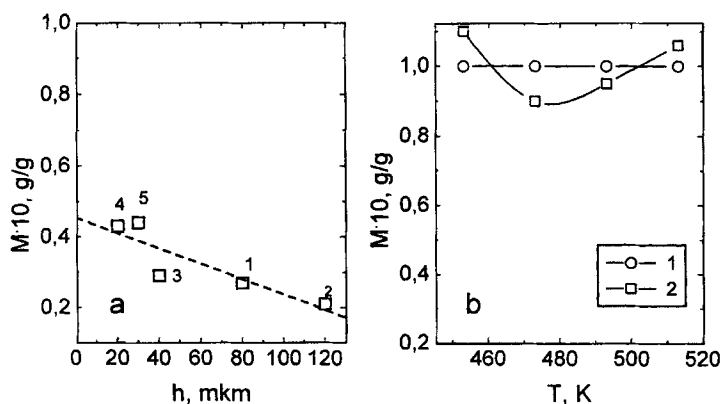


FIGURE 3 Sorption capacity (a) of coatings in hexane vs. transcrystalline layer extent at the formation temperature of: 433 K (1), 453 K (2), 473 K (3), 493 K (4), 513 K (5). Hexane sorption capacity (b) vs. formation temperature for rapidly (1) and slowly (2) cooled coatings.

observed for slowly cooled BTL-free coatings. In this case M^∞ correlates with the density in agreement with the currently available data [14] (Fig. 3, Tab. II). The diffusion coefficient D increases with the fall of density and with the changes in crystalline cell parameters.

Fast (130 K/min) cooling of the coating in water at 293 K changes structural and diffusive characteristics (Fig. 2, Tab. II). In such conditions polymer crystallization occurs at the same degree of cooling, as in the case above, but at a higher rate. In this case BTL do not generate, and the minimum of \bar{D} is observed at higher temperatures (473–493 K) and the absolute values of \bar{D} are comparable to the similar data for BTL containing samples (Fig. 2). It should be noticed that the crystallinity of the above mentioned samples does not correlate with the integral density (Tab. II).

This suggests that the temperature of film formation at given conditions of sample cooling affects the crystallinity and the amorphous regions density ambiguously. The calculation of the latter parameters with the help of Eq. (1) shows their difference depending upon T (Tab. II). So the character of \bar{D} changes for the fast cooled samples appears to be determined by the summary contribution of φ_C and d_a depending upon T ambiguously. Thus, \bar{D} is not associated only with a single structural parameter. The sorption density of fast cooled coatings is essentially independent of T (Fig. 3, b). Our study revealed that the value of M^∞ approaches the literary data [14] for corresponding

TABLE II Structural characteristics of polyethylene coatings

| T, K | Elementary cell parameters, nm | | $d, \text{kg/m}^3$ | $d_a, \text{kg/m}^3$ | $\varphi_C, \%$ |
|--|--------------------------------|-------|--------------------|----------------------|-----------------|
| | a | b | | | |
| Cooling rate of BTL-free coatings: 15 K/min | | | | | |
| 433 | 0.74 | 0.481 | 922.8 | — | — |
| 453 | 0.74 | 0.482 | 925.0 | 861.0 | 39.0 |
| 473 | 0.75 | 0.513 | 924.9 | — | — |
| 493 | 0.75 | 0.514 | 924.3 | — | — |
| 513 | 0.76 | 0.506 | 923.7 | — | — |
| Cooling rate of BTL-free coatings: 130 K/min | | | | | |
| 433 | — | — | 917.6 | 881.6 | 30.4 |
| 453 | — | — | 917.5 | 870.8 | 36.1 |
| 473 | — | — | 918.7 | 877.3 | 33.7 |
| 493 | — | — | 921.3 | 880.5 | 34.1 |
| 513 | — | — | 920.7 | 871.2 | 31.1 |

crystallinity and differs slightly from similar values for slowly cooled BTL-free coatings (Fig. 3, a). The fall of \bar{D} in the fast cooled coatings as compared to slowly cooled samples without BTL may cause amorphous regions sealing. So in the minimum of \bar{D} ($T = 473 - 493$ K) the density of amorphous regions is $877 - 891$ kg/m³ being above similar value of 861 kg/m³ for slowly cooled samples without BTL. In this case the coating formation at different temperatures and their hardening essentially change \bar{D} but have no effect on M^∞ .

The integral diffusion coefficient of CO₂ for BTL containing coatings changes with T similarly to \bar{D} of hexane. However, it should be noted that their values are different (Fig. 4). It is likely that BTL increase the diffusion of CO₂ to a less degree than that of hexane. The magnitude of \bar{D} for water vapour passes through the minimum at 453 K for the coatings formed at various T and cooled at a rate of 15 and 130 K/min (Fig. 5). The values of \bar{D} for hardened samples are less than those for slowly cooled ones but this difference is smaller than in the case of hexane. In doing so, some growth of \bar{D} as the integral density and the density of amorphous regions increase is observed for hardened coatings (Fig. 2, Tab. II). It is obvious that \bar{D} changes

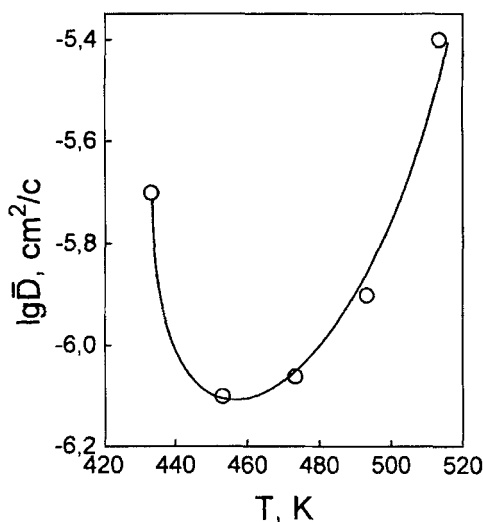


FIGURE 4 Integral CO₂ diffusion coefficient vs. formation temperature for slowly cooled coatings with a transcrystalline layer.

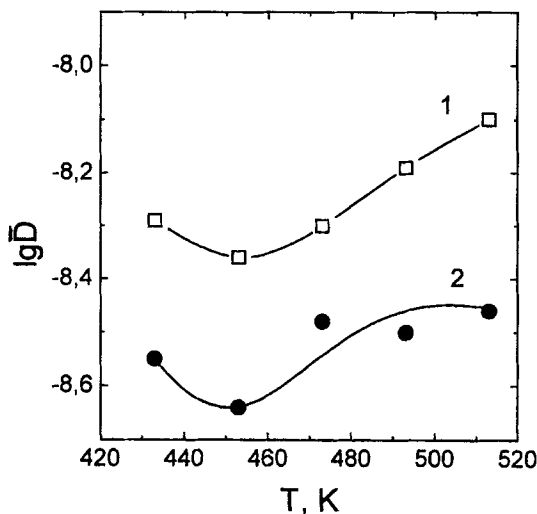


FIGURE 5 The effect of formation temperature for a coating without a transcrystalline layer on the integral diffusion coefficient of water vapor. 1 – air cooling at the rate of 15 K/min; 2 – water cooling at the rate of 130 K/min.

revealed for water vapour are due not only to the structural peculiarities but also to the thermodynamic of interaction in the polymer-sorbate system [3]. The degree of oxydation increases with T [15].

Thus, the relationships obtained for systems under study confirm the previously advanced thesis that temperature and temporal conditions of film formation and polyethylene coating crystallization essentially affect the structure and the protective characteristics of coating. Coating formation under the conditions bringing about the generation of extensive BTL favours the decrease in the diffusion coefficient of low molecular-weight compounds in polyethylene coatings. The fall in diffusion coefficient is more pronounced for hexane and water vapour and less for CO_2 . This is accompanied by a drop in sorptive capacity of the coating. At the same time, the diversity and ambiguity of structural changes in coatings in response to technological factors give no way of relating the diffusion properties to any single structural parameter, *e.g.*, crystallinity. From a practical point of view, technological parameters are convenient to use. The experimental evidence points to the face that the film formation temperature of 453 K is optimal for LDPE coating production.

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